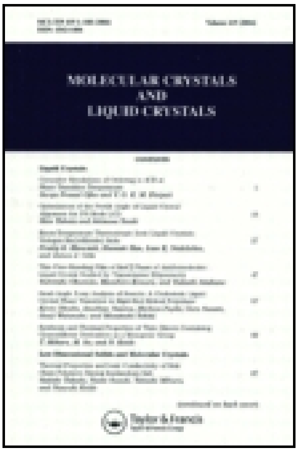

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ELECTRO-OPTIC INVESTIGATIONS IN SOME MOLECULAR-IONIC CRYSTALS

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Abstract The dispersion of second order optical susceptibility $\chi^{(2)}$ in molecular-ionic crystals is discussed. Examples of measurements and calculations of electro-optic coefficients in function of frequency for molecular-ionic crystals are presented.

INTRODUCTION

The nonlinear optical (NLO) crystals possessing electro-optical (EO) properties are widely used for construction of many optoelectronic devices such as modulators, switches and optical signal processors. Up to date, however, only ionic and semiconductor type materials have found serious applications in electrooptics. It is well known that many organic molecular materials: crystals, polymers or Langmuir-Blodgett films show excellent NLO properties [1,2] surpassing those of inorganics, especially with respect to speed as well as magnitude of nonlinear response. The main problem in their wide implementation is still difficult fabricability, unsatisfactory chemical stability and optical quality.[3]

Here we present study of EO properties of materials which could be classified as molecular-ionic crystals. The ionic character of these compounds comprising easily polarizable organic molecules and inorganic ions can result in materials of good optical quality and stability without loosing the magnitude and speed of NLO response to the irradiation.

LINEAR ELECTRO-OPTIC (POCKELS) EFFECT

The linear electro-optic (Pockels) effect is the variation of refractive index n of an NLO material when an electric field is applied across the material. This second order nonlinear effect is described by susceptibility tensor $\chi^{(2)}_{ijk}(-\omega;\omega,0)$, where 0 conventionally corresponds to a frequency of an externally applied electric field and ω is the angular frequency of the light wave. The knowledge of dispersion properties of a general $\chi^{(2)}_{ijk}(-\omega_3;\omega_1,\omega_2)$ tensor for NLO crystal is crucial for understanding the physics of NLO response and opens the possibility to optimize the material properties by molecular engineering.

The Pockels effect usually is measured with a dc electric field or ac one at low frequencies (< 20 kHz) then it comprises all possible contributions to $\chi^{(2)}_{ijk}(-\omega;\omega,0)$ tensor:[4] *electronic* (estimated from second harmonic generation, SHG experiment), *lattice optic vibrations* (estimated from studies of polar phonons by Raman and infrared spectroscopy) and *piezoelectric-photoelastic* (calculated on a basis of piezoelectric strain tensor d_{ijk} and elastooptic (strain-optical) tensor p_{ijkl}). The signs of individual contributions can be determined by measuring the dispersion of the EO effect with electric field frequencies near acoustic, optic and electronic resonances.

For the discussion of EO properties we use the more common electro-optic r coefficients and the change in the optic index ellipsoid is written as:

$$\Delta(n^{-2})_{ij} = r^{T}_{ijk}\, E_k = (r^{s}_{ijk} + p_{ijlm}\, d_{lmk})E_k \qquad (1)$$

where T and s indicate constant stress and strain respectively and p and d are the elastooptic and piezoelectric strain tensors, E_k is the component of electric field. The so called clamped electro-optic coefficients r^{s}_{ijk} can be calculated if the respective tensors r^{T}_{ijk}, p_{ijlm} and d_{lmk} are known or measured directly at frequencies of ac field well above piezoelectric resonances of a sample.

The clamped EO coefficients r^{s}_{ijk} can be split into purely electronic part r^{el}_{ijk} and r^{o}_{ijk} - the optical phonon contribution due to polar vibrational modes being both Raman and infrared active. According to [5]:

$$r^{el}_{ijk} = - \frac{2\chi^{(2)}_{ijk}(-2\omega;\omega,\omega)}{n^2_{ii}(\omega)\, n^2_{jj}(\omega)} \qquad (2)$$

and can be evaluated from SHG experiment. On the other hand r^o_{ijk} can be expressed [6] as $\alpha^m_{ijk}Q^m_kE_j$ i.e. by the change in i component of optical polarization per unit volume due to lattice displacements $Q^m_k = \beta^m_k E_k$ where summation over repeated indices is understood. In the above expression Q^m_k is the instantaneous amplitude of a polar mode with angular frequency ω_m and lattice displacement along k and α^m_{ijk} is the differential polarizability. Alternatively r^o_{ijk} can be written as: [6]

$$r^o_{ijk} = (\varepsilon_o n^2_{ii} n^2_{jj})^{-1} \left[\pm \left\{ \sum_m \alpha^m_{ijk} \left[\frac{\varepsilon_o \Delta\varepsilon^m_k v}{K^m_k} \right]^{1/2} \right\} \right] \qquad (3)$$

where $\Delta\varepsilon^m_k$ is the contribution of the m-th mode to the low frequency dielectric permittivity, v is the unit cell volume and K^m_k is the spring constant of the m mode. Basing on simplified theory of Fredrickson et al.[7] one can calculate the ratio r^o_{ijk}/r^e_{ijk} for a polar crystal providing the polarized Raman and infrared spectra are known (e.g. frequency and intensities of LO and TO modes).

RESULTS AND DISCUSSION

Our investigations of electro-optic properties are limited to two groups of mm2 point symmetry crystals:

i) sodium, potassium and rubidium acid phthalates (NaAP, KAP, RbAP) which are pyroelectric,

ii) $(CH_3NH_3)_5Bi_2Cl_{11}$ (PMACB) and $(CH_3NH_3)_5Bi_2Br_{11}$ (PMABB) which are ferroelectric at room temperature.

Pockels coefficients were measured employing two dynamical methods: elctromodulation technique (with internal light interference)[8] and Mach-Zehnder interferometric one (with external light interference)[9]. The basic experimental system constructed by us is shown schematically in Fig. 1. The mutual phase difference between two laser beams was conveniently changed by an introduction into one arm of an interferometer a cuvette with slowly cooled water. This enabled us to monitor maximal electro-optic modulation which occurs periodically whenever the phase difference between two beams is equal $\Delta\Gamma = m\,\frac{\pi}{4}$, where m is an odd number.

Employing configuration with external electric field applied along the polar axis c ($E_3 \neq 0$) and with k vector of light along the b or a axes one can establish either single coefficients r^T_{333}, r^T_{223} and r^T_{113} or figures of merit such as $\frac{1}{2}(n^3_{33}r^T_{333} - n^3_{22}r^T_{223})$etc. [10,11]. Combination of the mentioned two techniques allows for determination of relative sign of Pockels effect coefficients [12].

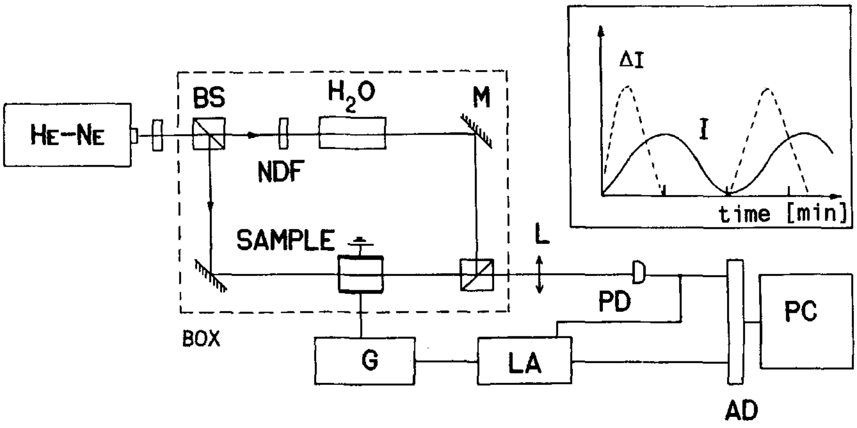

FIGURE 1 Experimental set up with Mach-Zehnder interferometer. G - signal generator (1 Hz - 1MHz), LA - lock-in amplifier, AD - analog-digital card, PC - personal computer, PD - fast photodiode, M - mirror, BS - beam splitter, NDF - neutral density filter, L - lens.

Measurements performed at room temperature, λ = 632.8 nm, ν = 10 kHz show that the considered materials exhibit considerable EO coefficients (cf. TABLE I).

The constant strain EO coefficients r^s could only be calculated for KAP for which the necessary p_{ijkl} [13] and d_{ikl} [14] tensors has been measured. As is seen from the Table I the r^s EO coefficients for KAP are considerably smaller than r^T ones. The similar relative decrease of

TABLE I EO coefficients of some molecular-ionic crystals

Compound	EO effective or single coefficient	
PMACB	$r_a^{eff} = r^T_{333} - (n_2/n_3)^3\ r^T_{223} \cong 18.8$ pmV^{-1}	
PMABB	$r_a^{eff} = r^T_{333} - (n_2/n_3)^3\ r^T_{223} \cong 5.8$ pmV^{-1}	
NaAP	$r^T_{113} = 2.8$ pmV^{-1}	
KAP	$r^T_{113} = 5.3$ pmV^{-1}	$r^s_{113} = 1.0$ pmV^{-1}
	$r^T_{333} = 7.1$ pmV^{-1}	$r^s_{333} = 2.3$ pmV^{-1}
RbAP	$r^T_{113}\ \square\ 9.1$ pmV^{-1}	

EO coefficients r^s versus r^T have been reported for $BaTiO_3$ [15] and $KNbO_3$ [16]. The typical figure of merit for a transverse light modulator $\frac{1}{2}(n_3^3 r_{33} - n_1^3 r_{13})$ calculated for KAP on the basis of r^T coefficients amounts to -0.45 pmV^{-1} whereas that calculated with r^s coefficients amounts to $+1.51$ pmV^{-1}. This means that apart of sign change the crystal will work better at higher frequencies (above piezoelectric resonances) than at low frequencies. The change of sign of this figure of merit has been confirmed by an experiment allowing monitoring of dispersion of EO coefficients in the region of piezoelectric resonances (cf. Fig. 2).

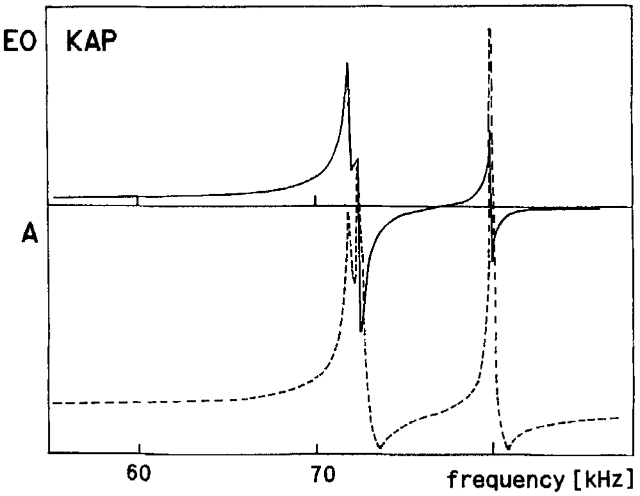

FIGURE 2 The example of dispersion of EO coefficients $\frac{1}{2}(n_3^3 r_{33} - n_1^3 r_{13})$ (sold line) and amplitude of piezoelectric resonance (dashed line) for KAP in the vicinity of the lowest piezoelectric resonances of the sample.

The dispersion in the region of lattice vibrational modes can be probed by fitting the far infrared polarized reflectivity spectra of KAP [19]. From the fit one can obtain the intensities and frequencies of the LO and TO modes. This according to Fredrickson et al. [7] is sufficient to estimate the contribution of lattice polar modes to r^{s} EO coefficients by calculating the r^{o}/r^{el} value. The calculation performed by us give for the ratio r^{o}_{113}/r^{el}_{113} four values (due to sign uncertainties): 26%, 16%, 34% and 21% . From the above investigations one can conclude that the lattice contribution constitutes in average 24 percents of r^{s}_{113} EO coefficient. The SHG experiment for KAP has not been performed until now.

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